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SUPERCONDUCTIVITY IN NONSTOICHIOMETRIC COMPOUNDS.(U)
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SUPERCONDUCTIVITY IN NONSTOICHIOMETRIC COMPOUNDS

by

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SUMMARY

The objective of this research is to examine the effect of changing chemical composition on the properties of superconducting chemical compounds. Compounds likely to be superconducting are synthesized; properties are investigated as functions of departure from stoichiometry and cation-for-cation or anion-for-anion substitution. The special role of localized magnetic moments on quenching superconductivity is examined.

During the report period, the following compounds have been prepared: $Nb_{1+x}S_2$, $HfTe_x$, HfI_xS_{2-x}, HfS_2, Nb-doped VSe_2, $MoS_{2-x}Se_x$, $SnS_{2-x}Se_x$, YB_6, $Pb_xMo_6S_{8-y}$, and $Tb_xYb_3S_6$. Preliminary findings are as follows:

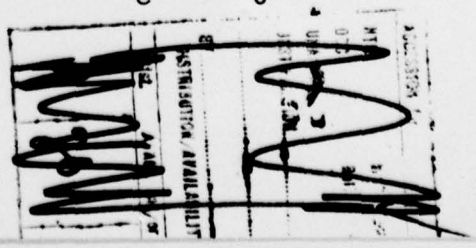
(a) $Nb_{1+x}S_2$ (Wayne Fisher) During the past year we have made a concentrated effort to synthesize precisely stoichiometric NbS_2 and establish the conditions under which the various polytypes can be obtained. It appears that the material most often described in the literature is $Nb_{1.05}S_2$. The effect of quench temperature, reaction temperature, and sulfur pressure has been examined. Changing quench temperature between 1000° and 750°C gives only the 3R polytype $Nb_{1.08}S_2$. Raising the excess sulfur pressure from 0 to 15 atm (quench from 750°C) reduces x in $Nb_{1+x}S_2$ from 0.14 to 0.01, all of the 3R polytype The best $Nb_{1+x}S_2$ we have been able to make is $Nb_{1.01}S_2$. The 2H polytype appears to be high nonstoichiometric.

(b) $HfTe_x$ (Dave Hodul) The tendency of stoichiometry deviation on going from S to Se to Te appears to be opposite for the IVB from the VB elements. Whereas, TiS_2 is very difficult to make stoichiometric, $TiTe_2$ is easily always on stoichiometry. To the contrary, HfS_2 is easily made stoichiometric, but $HfTe_x$ is nonstoichiometric ($1.7 < x < 1.9$). Precision density and structure studies have been made to identify the nature of the defect. It appears that the major defect is tellurium vacancies with hafnium progressively substituting on an antistructure site. Conductivity and ESR studies are in progress. Iodine-substituted hafnium disulfide has also been made over the range $0 < x < 0.6$ in HfI_xS_{2-x}. The structure is 1T polytype throughout.

(c) $Nb_{0.05}V_{0.95}Se_2$ (Lynn Schneemeyer) Stoichiometric VSe_2 is not superconducting but shows a charge-density-wave transition at 110°K. Large (70%) substitution doping of Nb for V raises the onset temperature to about 230°K, opposite in direction to that reported for other doping elements. As part of a concentration-dependence study we have synthesized $Nb_{0.05}V_{0.95}Se_2$ and carefully measured its magnetic susceptibility over the range 1.5 - 300°K. Two transitions have been observed: one at 119°K (probably onset of incommensurate CDW) and the other at 82°K (probably lock-in to commensurate CDW). A totally unexpected finding was the persistence of plateaus for ~10° in the susceptibility vs. T curve at both transitions. The effects are reversible and reproducible, and the reason for them is being investigated.

(d) $MoS_{2-x}Se_x$ and $SnS_{2-x}Se_x$ (Lynn Schneemeyer) A full range of closely-spaced samples has been synthesized and investigated for X-ray structure. The molybdenum series shows an anomalously metallic behavior in the middle of the series, whereas the end members are clearly semiconducting. Both series show highly unusual behavior in the c/a parameter with a clear maximum in the c/a vs. x curve at x = 1.2 for $MoS_{2-x}Se_x$ and x = 0.7 for $SnS_{2-x}Se_x$. The former series is the 2H polytype throughout; the latter, 1T. The reason for the breakdown of Vegard's law is not known. Intercalation experiments with NH_3 and CH_3NH_2 are in progress. The tin series has been sent to Prof. Rolfe Herber at Rutgers for collaborative Mössbauer studies.

(e) YB_6 (Rudi Sobczak) In an attempt to understand why the T_c of $La_xY_{1-x}B_6$ decreases with x, although the electron concentration is not changing, we have initiated a systematic study of χ vs. T and T_c vs. composition for the mixed trivalent hexaborides. The major problem is in the quality of the boron used for the preparation. The amorphous boron, which reacts in the rf-induced synthesis most smoothly, contributes the most iron. For YB_6, we have found a linear depression in T_c with iron content, which extrapolates back to 6.5°K for no iron. Surprisingly, a small impurity of yttrium also depresses T_c. The observed extremely low T_c of LaB_6 (0.122°K instead



of a predicted value in the range 24 to 67°K) is tentatively attributed to partial electron localization involving a mixed valence state.

(f) $Pb_xMo_6S_{8-y}$ (Frank Delk) In an attempt to investigate the effect on T_c of departure from stoichiometry, we have explored the conditions required to make $PbMo_6S_8$, for which the T_c is reported at 15.2°K. Variation of thermal conditions and sulfur pressure has failed to give the stoichiometric product. Attempts to grow single crystals have also been unsuccessful. It appears that the reported materials are, in reality, mixtures, and the precise identity of the superconducting compound of maximum T_c is not known.

(g) $Tb_xYb_3S_6$ (Alex Chang) In collaboration with Professor Jean Flahaut at the University of Paris, we are examining the structure of the ternary chalcogenide resulting from reaction of Tb_2S_3 with Yb_2S_3. Two kinds of crystals, black and red, have been obtained. The black crystal has space group Pnam; the red $I\,4_1/amd$. The latter is a new phase for rare earth sulfides.

PERSONNEL

In addition to the principal investigator, Professor M. J. Sienko, the following people were associated with this project during the report period:

(a) Research Associate	Dr. Rudi Sobczak Dr. Peter Edwards
(b) Research Assistants	Alex Chang Frank Delk Wayne Fisher Dave Hodul Lynn Schneemeyer
(c) Secretary	Christina Fuiman

No Ph.D. degrees were completed during this period.

PUBLICATIONS

The following papers were published during the report period:

(1) "Conduction-electron spin resonance in metallic lithium", Pierre Damay and M. J. Sienko, Phys. Rev. B 13, 603-606 (1976).

(2) "Antiferromagnetic coupling in ytterbium-diluted dysprosium hexaborides", Jerry L. Krause and M. J. Sienko, J. Chem. Phys. 64, 4265-4268 (1976).

(3) "Synthesis and Structural Aspects of the Vanadium-Substituted Niobium Diselenides", Michel Bayard, Bernard F. Mentzen, and M. J. Sienko, Inorg. Chem. 15, 1763-1767 (1976).

(4) "Preparation and X-ray Study of Mixed-Anion Tungsten Dichalcogenides", B. F. Mentzen and M. J. Sienko, Inorg. Chem. 15, 2198-2202 (1976).

(5) "Electrical and Magnetic Properties of Vanadium-Substituted Niobium Diselenides", M. Bayard and M. J. Sienko, Journal de Physique 37(C4), 169-174 (1976).

(6) "Anomalous Electrical and Magnetic Properties of Vanadium Diselenide", M. Bayard and M. J. Sienko, J. Solid State Chem. 19, 325-330 (1976).

INTERACTIONS

lecture at Rutgers University (3/30/76) on "Strange Properties of Metal-Ammonia Compounds"

lecture at College of William & Mary (4/1/76) on "Strange Behavior of Sodium in Liquid Ammonia"

lecture at College of William & Mary (4/2/76) on "Layered Compounds, Tunnels, and the Chemical Control of Superconductivity"

external reviewer at Iowa State University on Materials Science Program, Ames Lab - ERDA (5/19/76 - 5/21/76)

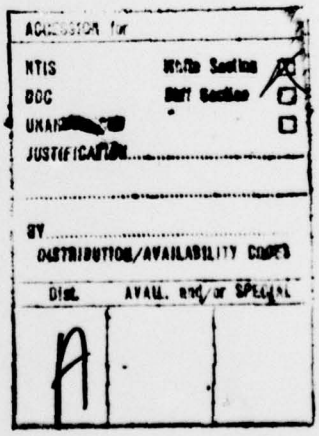
lecture at Vth International Conference on Solid Compounds of Transition Elements Uppsala, on "Vanadium-Substituted Niobium Diselenides" (6/25/76)

paper presented at Colloque International du CNRS sur Les Transitions Metal-Nonmetal at Autrans, France, on "Effect of Vanadium Substitution on the Electric and Magnetic Properties of Niobium Diselenide" (6/28/76)

Interactions cont'd.

paper presented at Gordon Conference, Inorganic Chemistry, on "Electric and Magnetic Anomalies in VSe_2" (8/3/76)

paper presented at ACS National Meeting, San Francisco, on "Electron Spin Resonance Studies of V_3O_7" (9/1/76)



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superconductivity
layered compounds
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Stoichiometry and polytype formation have been investigated in Nb disulfide over a range of preparation temperature and sulfur pressure. All the products are 3R and show an excess of Nb. The range of stoichiometry in Hf ditelluride has been established as 1.7-1.9 and the majority defect as Te vacancy. Magnetic studies on Nb-substituted V diselenide show CDW transitions at 119°K and 82°K. Mixed sulfide-selenides of Mo and of Sn show unusual maxima in c/a ratio versus composition. The effect of magnetic impurity on superconducting temperature of yttrium hexaboride has been examined.

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